

1                   **HYDROTREATING OF FISCHER-TROPSCH**  
2                   **DERIVED FEEDS PRIOR TO OLIGOMERIZATION**  
3                   **USING AN IONIC LIQUID CATALYST**  
4

5                   FIELD OF THE INVENTION  
6

7       This invention relates to the oligomerization of olefins in Fischer-Tropsch  
8       derived feeds by use of an ionic liquid oligomerization catalyst.  
9

10                  BACKGROUND OF THE INVENTION  
11

12       The economics of a Fischer-Tropsch complex has in the past only been  
13       desirable in isolated areas where it is impractical to bring the natural gas to  
14       market; however, a Fischer-Tropsch complex can benefit if the production of  
15       high-value products in the product slate, such as lubricating base oil and high  
16       quality diesel, can be increased. Fortunately, the market for lubricating base  
17       oils of high paraffinicity is continuing to grow due to the high viscosity index,  
18       oxidation stability, and low volatility relative to viscosity of these molecules.  
19       The products produced from the Fischer-Tropsch process contain a high  
20       proportion of wax which makes them ideal candidates for processing into  
21       lubricant base stocks. Accordingly, the hydrocarbon products recovered from  
22       the Fischer-Tropsch process have been proposed as feedstocks for preparing  
23       high quality lubricant base oils.  
24

25       If desired, high quality diesel products also may be prepared from the  
26       syncrude recovered from the Fischer-Tropsch process. Fischer-Tropsch  
27       derived diesel typically has very low sulfur and aromatics content and an  
28       excellent cetane number. In addition, the process of the present invention  
29       makes it possible to produce diesel having low pour and cloud points which  
30       enhance the quality of the product. These qualities make Fischer-Tropsch  
31       derived diesel an excellent blending stock for upgrading lower quality  
32       petroleum-derived diesel.

1 Accordingly, it is desirable to be able to maximize the yields of such higher  
2 value hydrocarbon products which boil within the range of lubricating base oils  
3 and diesel. At the same time, it is desirable to minimize the yields of lower  
4 value products such as naphtha and C<sub>4</sub> minus products. Unfortunately, most  
5 Fischer-Tropsch processes produce lower molecular weight olefinic products  
6 within the C<sub>3</sub> to C<sub>8</sub> range. It is advantageous in a Fischer-Tropsch operation to  
7 increase the yield of higher boiling products and also increase the amount of  
8 branching in the molecules.

9  
10 The average molecular weight of the hydrocarbon molecules present in the  
11 Fischer-Tropsch material may be increased by the oligomerization of olefins  
12 present in the feed. Therefore, oligomerization may be used to increase the  
13 yield of higher boiling products, such as lubricating base oils and diesel, and  
14 to lower the yield of lower boiling products, such as LPG and naphtha, from  
15 the Fischer-Tropsch process. Oligomerization also introduces desirable  
16 branching into the hydrocarbon molecule which lowers the pour point of the  
17 diesel and lubricating base oil products thereby improving the cold flow  
18 properties of the product. For those Fischer-Tropsch products intended as  
19 feed for a hydrocracking operation, a further advantage is that the branching  
20 renders the molecule easier to crack. U.S. Patent No. 4,417,088 describes a  
21 process for oligomerizing olefins to produce molecules having desirable  
22 branching. Recently, the use of ionic liquid catalysts has been proposed for  
23 use in the oligomerization of olefins. See, for example, U.S. Patent  
24 Nos. 5,304,615 and 5,463,158. See also European Patent Application  
25 No. 0791643 A1. U.S. Patent No. 6,395,948 teaches that the oligomerization  
26 of alphaolefins using an ionic liquid catalyst must be conducted in the  
27 absence of an organic diluent if a polyalphaolefin having a high viscosity is  
28 desired.

29 Most Fischer-Tropsch derived materials as they are recovered from the  
30 Fischer-Tropsch plant will contain a certain amount of oxygenates, mostly as  
31 alcohols, but also lesser amounts of other oxygenates such as, for example,  
32 aldehydes, ketones, anhydrides, and carboxylic acids. In processes intended

1 for upgrading the Fischer-Tropsch materials by oligomerization, the alcohols  
2 may be readily converted to olefins by dehydration, and the minor amounts of  
3 the other remaining oxygenates were not believed to be present in sufficient  
4 quantity to interfere with additional downstream processing. However, it has  
5 been found that when ionic liquid catalysts are used in the oligomerization  
6 step, even very small amounts of oxygenates will deactivate the catalyst. The  
7 present invention is intended to address this problem.

8  
9 Most, but not necessarily all, of the oxygenates from the Fischer-Tropsch  
10 process will be included in the condensate fraction recovered from the unit. As  
11 used in this disclosure, the term "Fischer-Tropsch condensate" refers  
12 generally to the C<sub>5</sub> plus fraction which has a lower boiling point than the  
13 Fischer-Tropsch wax fraction. That is to say, the condensate represents that  
14 fraction which is normally liquid at ambient temperature. Fischer-Tropsch  
15 condensate may be obtained directly from the Fischer-Tropsch plant or  
16 produced from the Fischer-Tropsch wax by use of a wax hydrocracker.  
17 "Fischer-Tropsch wax" refers to the high boiling fraction from the  
18 Fischer-Tropsch derived syncrude and is most often a solid at room  
19 temperature.

20  
21 As used in this disclosure, the words "comprises" or "comprising" are intended  
22 as an open-ended transition meaning the inclusion of the named elements,  
23 but not necessarily excluding other unnamed elements. The phrases "consists  
24 essentially of" or "consisting essentially of" are intended to mean the  
25 exclusion of other elements of any essential significance to the composition.  
26 The phrases "consisting of" or "consists of" are intended as transitions  
27 meaning the exclusion of all but the recited elements with the exception of  
28 only minor traces of impurities.

## 29 30 BRIEF DESCRIPTION OF THE INVENTION

31  
32 In its broadest aspect, the present invention is directed to a process for  
33 oligomerizing a Fischer-Tropsch derived feed containing oxygenates which

1 comprises (a) reducing significantly the oxygenates present in the  
2 Fischer-Tropsch derived feed by contacting said feed with a hydrotreating  
3 catalyst under hydrotreating conditions in a hydrotreating zone and recovering  
4 from the hydrotreating zone a Fischer-Tropsch derived hydrotreated feed  
5 which contains a significantly reduced amount of oxygenates as compared to  
6 the Fischer-Tropsch derived feed and also a significant amount of paraffins;  
7 (b) pyrolyzing the Fischer-Tropsch derived hydrotreated feed in a thermal  
8 cracking zone under thermal cracking conditions pre-selected to crack the  
9 paraffin molecules to form olefins and collecting an olefin-enriched  
10 Fischer-Tropsch feed from the thermal cracking zone; (c) contacting the  
11 olefin-enriched Fischer-Tropsch feed with a Lewis acid ionic liquid catalyst in  
12 an oligomerization zone under oligomerization reaction conditions; and  
13 (d) recovering from the oligomerization zone a Fischer-Tropsch derived  
14 product having molecules characterized by a higher average molecular weight  
15 and increased branching as compared to the Fischer-Tropsch derived feed.

16  
17 It has been found that oxygenates present in Fischer-Tropsch derived feeds  
18 interfere with the ability of an ionic liquid oligomerization catalyst to promote  
19 the oligomerization of the olefins, i.e., they deactivate the catalyst.  
20 Surprisingly, this interference was found to occur even when the  
21 Fischer-Tropsch feed is first subjected to a dehydration step which converts  
22 substantially all of the alcohols present into olefins. It has been discovered  
23 that even low levels of other oxygenates, such as ketones and carboxylic  
24 acids, and even low levels of residual alcohols which remain in the  
25 condensate after the dehydration step will deactivate the ionic liquid catalyst.  
26 In some cases one mole of oxygenate can deactivate one mole of catalyst.  
27 Therefore, in the present invention, a hydrotreating step is employed to  
28 reduce the amounts of the oxygenates in the Fischer-Tropsch feed intended  
29 to be sent to the oligomerization operation when an ionic liquid catalyst is  
30 employed. The entire syncrude product from the Fischer-Tropsch plant, that is  
31 to say, both the condensate and the wax fraction may be hydrotreated in the  
32 present invention. In different processing schemes within the scope of the  
33 invention, only the wax fraction or the condensate fraction may be

1 hydrotreated. In other embodiments of the invention, only a part of one or both  
2 of the fractions may be hydrotreated. The only limitation to the material being  
3 hydrotreated being the reduction of the oxygenates in the feed being sent to  
4 the oligomerization operation to a low enough level to prevent their  
5 interference with the production of the desired product slate. In carrying out  
6 the hydrotreating operation, the hydrotreating catalyst employed and the  
7 hydrotreating conditions are selected to minimize the cracking of the  
8 hydrocarbon molecules while converting the oxygenates.

9  
10 Since hydrotreating will saturate the double bonds present in the hydrocarbon  
11 molecules, following the hydrotreating step, the hydrotreated Fischer-Tropsch  
12 derived feed is pyrolyzed in a thermal cracking zone under thermal cracking  
13 conditions pre-selected to crack the paraffin molecules to create olefins prior  
14 to oligomerization. In one embodiment of the invention, the hydrotreated  
15 Fischer-Tropsch derived feed is steam cracked in a flow through reactor.

16  
17 Following thermal cracking or pyrolysis, the olefin-enriched Fischer-Tropsch  
18 feed is oligomerized using an effective oligomerizing amount of a Lewis acid  
19 ionic liquid catalyst.

20  
21 Following oligomerization, the Fischer-Tropsch derived product is dewaxed, if  
22 needed, to improve the cold flow properties of the products. In addition, it is  
23 usually desirable to saturate the remaining double bonds in the hydrocarbon  
24 molecules of the Fischer-Tropsch derived products. This latter operation,  
25 referred to herein as hydrofinishing, improves the UV and oxygen stability and  
26 color of the products.

27  
28 The present invention also makes possible the production of higher quality  
29 lubricant base oil or a higher quantity of higher viscosity lubricant base oil than  
30 can be made by catalytic isomerization dewaxing of Fischer-Tropsch wax  
31 alone. In conventional Fischer-Tropsch operations, the amount of high  
32 viscosity lubricant base oil that can be produced by isomerization is limited by  
33 the amount of high molecular weight molecules present in the wax fraction.

1 Oligomerization provides a method to create more high molecular weight  
2 molecules and thus more high viscosity lubricant base oil.

### 3 4 BRIEF DESCRIPTION OF THE DRAWINGS

5  
6 Figure 1 is a schematic representation shown in block diagram illustrating one  
7 embodiment of the invention in which both the condensate fraction and the  
8 wax fraction from the Fischer-Tropsch unit are passed to the hydrotreating  
9 zone.

10  
11 Figure 2 is a schematic representation of an alternate embodiment of the  
12 invention in which only the wax fraction from the Fischer-Tropsch unit is  
13 passed to the thermal cracking and oligomerization units.

14  
15 Figure 3 is a schematic representation of an embodiment of the invention in  
16 which the Fischer-Tropsch condensate fraction is passed to the thermal  
17 cracking and oligomerization units.

### 18 19 DETAILED DESCRIPTION OF THE INVENTION

20  
21 The present invention will be more clearly understood by referring to Figure 1  
22 which illustrates a simplified processing scheme showing the elements of the  
23 invention. Two separate Fischer-Tropsch feed streams are shown leaving the  
24 Fischer-Tropsch unit 2. They include a Fischer-Tropsch condensate feed 4  
25 and a Fischer-Tropsch wax feed 6 shown as being carried to the hydrotreating  
26 unit 8 where the oxygenates and any nitrogen compounds in the feed streams  
27 are removed. In the hydrotreating unit, most of the unsaturated bonds in the  
28 hydrocarbon molecules are also saturated. The hydrotreated Fischer-Tropsch  
29 derived feed comprising a mixture of both the condensate and wax fractions is  
30 collected in line 10 and carried to the thermal cracking unit 12 where the  
31 paraffin molecules are cracked to form olefins. The olefin-enriched  
32 Fischer-Tropsch feed from the thermal cracker is carried by line 14 to the  
33 oligomerization unit 16 where the feed is contacted with an ionic liquid catalyst

1 in order to increase the average molecular weight of the hydrocarbon  
2 molecules in the feed and introduce desirable branching into the molecule.  
3 The effluent from the oligomerization operation is carried by line 18 to the  
4 dewaxing unit 20 where the feed is dewaxed in order to further improve the  
5 flow properties of the product. The dewaxed product is sent via line 22 to a  
6 hydrofinishing unit 24 to saturate any remaining double bonds and improve  
7 the stability of the product. The hydrofinished product is sent by line 26 to the  
8 atmospheric and vacuum distillation unit 28 where the various products are  
9 separated. Shown in the figure exiting the distillation unit are the gaseous light  
10 products 30 which comprise the C<sub>4</sub> minus hydrocarbons, those hydrocarbons  
11 boiling within the range of naphtha 32, a diesel product 33, base oil  
12 products 34, and bottoms 36. The present scheme is intended to maximize  
13 the production of the higher value diesel and base oil products while  
14 minimizing the production of the gaseous light products. The bottoms fraction  
15 may be a heavy neutral base oil or bright stock or may be sent to another  
16 hydroprocessing unit for additional processing, if desired.

17 In the process scheme illustrated in Figure 1, the condensate and wax  
18 fractions may be processed together (commingled). Alternately, the  
19 condensate and wax fractions may be processed in any of the steps in  
20 separate blocks in the same equipment or processed in separate reactors.  
21 The objective is to process each fraction at optimum conditions to maximize  
22 the yields and/or desirable properties of the desired products.

23

24 The process scheme illustrated in Figure 1 shows both the condensate  
25 fraction and the wax fraction passing from the Fischer-Tropsch unit 2 to the  
26 hydrotreating, thermal cracking, and oligomerization units. Alternate  
27 embodiments of the invention may separate the condensate fraction and wax  
28 fraction and only one or the other of these fractions may pass to these units.  
29 For example, in order to minimize the amount of transportation fuel, especially  
30 naphtha, and maximize lubricant production, only the condensate fraction may  
31 pass to the hydrotreating, thermal cracking, and oligomerization units. In this  
32 embodiment, the wax fraction may pass directly to a dewaxing unit, with or

1 without being hydrotreated first. In a different embodiment, only the wax  
2 fraction may be passed to the hydrotreating, thermal cracking, and  
3 oligomerization units with the condensate fraction passing directly to an  
4 atmospheric distillation unit, with or without first being hydrotreated, to collect  
5 the naphtha and diesel products. Alternate embodiments employing the  
6 invention in various processing schemes are further illustrated in Figures 2  
7 and 3 which will further clarify how the invention may be used to produce  
8 different product slates, without limiting the scope of the invention.

9  
10 Figure 2 illustrates an alternate embodiment of the invention which is intended  
11 to produce lubricating base oil products having a high average molecular  
12 weight. The embodiment shown in Figure 2 is suitable for the production of  
13 base oils from which a Fischer-Tropsch derived bright stock may be prepared.  
14 It is also suitable for the production of high yields of base oils having a higher  
15 viscosity than can be prepared by simply hydroisomerization dewaxing of  
16 Fischer-Tropsch wax. In this embodiment, the Fischer-Tropsch wax fraction  
17 and condensate fraction are recovered separately from the Fischer-Tropsch  
18 reactor (not shown). The Fischer-Tropsch wax fraction enters the wax  
19 hydrotreating unit 104 via feed line 102. In the wax hydrotreating unit, the  
20 amount of oxygenates and the nitrogen compounds present in the wax feed  
21 are reduced. The hydrotreated wax feed is carried by line 106 to a high  
22 pressure separator 108 where some lower boiling hydrocarbons, generally  
23 those boiling below about 650 degrees F (about 345 degrees C), are  
24 separated from the higher boiling base oil fractions. The hydrotreated lighter  
25 fraction comprising primarily hydrocarbons boiling within the range of  
26 transportation fuels, such as diesel and naphtha, is collected as overhead in  
27 line 110 and mixed with condensate carried from the Fischer-Tropsch reactor  
28 in line 112. The hydrotreated lighter fraction from the high pressure separator  
29 and the condensate fraction pass together to the condensate hydrotreating  
30 unit 114. The hydrotreated condensate fraction, which now includes the light  
31 fraction from the high pressure separator, is collected in line 116 which carries  
32 the condensate directly to the atmospheric distillation unit 118.



1    Returning to the high pressure separator, the higher boiling hydrotreated  
2    fraction is collected in line 120 and is divided into two hydrotreated heavy  
3    streams. One stream passes directly by line 122 to the dewaxing unit 124.  
4    The second stream passes by way of line 126 to a first storage tank 128  
5    before passing to the thermal cracking and oligomerization operation. The  
6    amount of the hydrotreated heavy hydrocarbons sent to either the thermal  
7    cracking operation or the dewaxing unit will depend upon the amount of very  
8    heavy base oil product desired in the final product slate. The more heavy wax  
9    fraction that is sent to the thermal cracker, the more heavy-end lubricant base  
10    oils can be produced. The hydrotreated heavy oil fraction stored in first  
11    storage tank 128 is sent by line 130 to the thermal cracking unit 132 in which  
12    some of the paraffins are pyrolyzed to significantly increase the amount of  
13    olefins present in the feed. The olefin enriched heavy feed is sent via line 134  
14    to the oligomerization unit 136 where the heavy feed is oligomerized in the  
15    presence of a Lewis acid ionic liquid catalyst. The oligomerized heavy feed is  
16    collected in line 138 and sent to a second storage tank 140.

17

18    The first and second storage tanks 128 and 140, respectively, allow the  
19    flexibility to operate the downstream dewaxing unit 124 in either block or bulk  
20    mode. In block mode, the dewaxing unit processes either hydrotreated  
21    Fischer-Tropsch wax (directly from the high pressure separator 108 by way of  
22    line 122) or oligomerization product (from storage second storage tank 140 by  
23    way of line 142). This mode allows the dewaxing conditions to be optimized  
24    for the specific feed to maximize dewaxing yield and product qualities. It also  
25    allows for the collection of separate base oils derived from oligomerization or  
26    dewaxing only.

27

28    In bulk dewaxing mode, the oligomerized product from line 142 and  
29    hydrotreated Fischer-Tropsch wax from line 122 are commingled and  
30    dewaxed together. The oligomerized heavy feed leaves the second storage  
31    tank by way of line 142 and is mixed with the heavy feed stream in line 122.  
32    This mixed heavy feed comprising both oligomerized heavy feed and heavy

1 feed coming directly from the high pressure separator passes to the dewaxing  
2 unit 124.  
3  
4 The product from the dewaxing unit is sent to the hydrofinishing unit 144 by  
5 line 146. In the hydrofinishing unit, the base oils are stabilized and collected in  
6 line 148 where they are mixed with the condensate fraction in line 116. The  
7 combined heavy and condensate fractions are carried by line 150 to the  
8 atmospheric distillation unit 118 where the overhead gases 152 are separated  
9 from the naphtha 154 and the diesel 156. The bottoms from the atmospheric  
10 distillation unit is collected in line 158 and passed to a vacuum distillation unit  
11 160 to separate the various base oil fractions. In the figure a light  
12 Fischer-Tropsch base oil product 162, a heavy Fischer-Tropsch base oil  
13 product 164, and a Fischer-Tropsch bottoms 166 are shown as being  
14 collected. The bottoms may be further refined to prepare bright stock if so  
15 desired and if necessary. If the bottoms product does not meet certain base  
16 oil specifications, such as pour point or cloud point, this stream may also be  
17 sent to the thermal cracking unit for further processing.  
18  
19 Figure 3 illustrates a different embodiment of the invention in which the  
20 Fischer-Tropsch condensate is oligomerized using the process of the  
21 invention. In this embodiment, the Fischer-Tropsch wax fraction is carried to  
22 the wax hydrotreating unit 202 by line 204. The hydrotreated wax fraction is  
23 recovered in line 206 and sent to a high pressure separator 208 where the  
24 wax is separated from a lighter fraction as already described in the description  
25 of Figure 2. The lighter fraction from the high pressure separator is collected  
26 by line 210 and mixed with the condensate fraction carried from the  
27 Fischer-Tropsch reactor in line 212. The mixture of condensate and light  
28 hydrocarbons from the high pressure separator are carried by common line  
29 214 to the condensate hydrotreating reactor 216 where substantially all of the  
30 oxygenates and the nitrogen compounds are removed. The oxygenate-free  
31 condensate is collected by outlet line 218 and divided into two streams. One  
32 stream passes directly to the atmospheric distillation unit 220 via line 222. The  
33 second stream passes by way of line 224 to a stripper 226 where the

1 C<sub>4</sub> minus hydrocarbons, ammonia, and water are removed. These overhead  
2 gases are collected by line 228 and sent to the atmospheric distillation  
3 unit 220. The condensate collected from the stripper passes by line 230 to the  
4 thermal cracker 232 where the paraffins are pyrolyzed to form olefins. The  
5 olefin-enriched condensate is carried via line 234 to the oligomerization  
6 unit 236. The oligomerized feed stream passes by way of line 238 to the  
7 condensate storage tank 240.  
8  
9 Returning to the high pressure separator 208, the hydrotreated heavy wax  
10 fraction is collected in line 242 and carried to hydrotreated wax storage tank  
11 244. The condensate storage tank 240 and hydrotreated wax storage tank  
12 244 allow the flexibility to operate the downstream dewaxing unit 246 in either  
13 block or bulk mode. In block mode, the dewaxing unit processes either  
14 hydrotreated Fischer-Tropsch wax (directly from the high pressure separator  
15 208 by way of wax storage tank 244 and line 248) or oligomerization product  
16 from condensate storage tank 240 by way of line 250). In bulk dewaxing  
17 mode, the oligomerized product from line 250 and hydrotreated  
18 Fischer-Tropsch wax from line 248 are commingled and dewaxed together.  
19  
20 The product from the dewaxing unit 246 is sent by line 252 to the  
21 hydrofinishing unit 254 and from there passes by way of line 256 to the  
22 atmospheric distillation unit 220. In the atmospheric distillation unit, the  
23 overhead gases 258, naphtha 260, diesel 262 are separately collected. The  
24 bottoms from the atmospheric distillation unit is collected in line 264 and sent  
25 to the vacuum distillation unit 266 where light base oil 268, medium base oil  
26 270, and bottoms 272 are shown as being separately collected.  
27  
28 The process scheme shown in Figure 3 is very flexible. The source of the  
29 condensate may be either condensate that is collected directly from the  
30 Fischer-Tropsch plant or hydrocrackate that is recovered from a wax  
31 hydrocracker. In the process scheme illustrated in Figure 3, the amount of  
32 base oils produced may be significantly increased as compared to the other  
33 process schemes described.

1 For clarity, the figures do not show hydrogen feed or recycle gas in the  
2 hydroprocessing units.

### 3 4 Fischer-Tropsch Synthesis

5  
6 During Fischer-Tropsch synthesis, liquid and gaseous hydrocarbons are  
7 formed by contacting a synthesis gas (syngas) comprising a mixture of  
8 hydrogen and carbon monoxide with a Fischer-Tropsch catalyst under  
9 suitable temperature and pressure reactive conditions. The Fischer-Tropsch  
10 reaction is typically conducted at temperatures of from about 300 degrees to  
11 about 700 degrees F (about 150 degrees to about 370 degrees C), preferably  
12 from about 400 degrees to about 550 degrees F (about 205 degrees to about  
13 290 degrees C); pressures of from about 10 to about 600 psia (0.7 to  
14 41 bars), preferably 30 to 300 psia (2 to 21 bars); and catalyst space  
15 velocities of from about 100 to about 10,000 cc/g/hr., preferably 300 to  
16 3,000 cc/g/hr.

17  
18 The products from the Fischer-Tropsch synthesis may range from C<sub>1</sub> to C<sub>200</sub>  
19 plus hydrocarbons with a majority in the C<sub>5</sub>-C<sub>100</sub> plus range. The reaction can  
20 be conducted in a variety of reactor types, such as, for example, fixed bed  
21 reactors containing one or more catalyst beds, slurry reactors, fluidized bed  
22 reactors, or a combination of different types of reactors. Such reaction  
23 processes and reactors are well known and documented in the literature. The  
24 slurry Fischer-Tropsch process, which is preferred in the practice of the  
25 invention, utilizes superior heat (and mass) transfer characteristics for the  
26 strongly exothermic synthesis reaction and is able to produce relatively high  
27 molecular weight paraffinic hydrocarbons when using a cobalt catalyst. In the  
28 slurry process, a syngas comprising a mixture of hydrogen and carbon  
29 monoxide is bubbled up as a third phase through a slurry which comprises a  
30 particulate Fischer-Tropsch type hydrocarbon synthesis catalyst dispersed  
31 and suspended in a slurry liquid comprising hydrocarbon products of the  
32 synthesis reaction which are liquid under the reaction conditions. The mole  
33 ratio of the hydrogen to the carbon monoxide may broadly range from about

1 0.5 to about 4, but is more typically within the range of from about 0.7 to about  
2 2.75 and preferably from about 0.7 to about 2.5. A particularly preferred  
3 Fischer-Tropsch process is taught in European Patent Application  
4 No. 0609079, which is completely incorporated herein by reference for all  
5 purposes.

6 Suitable Fischer-Tropsch catalysts comprise one or more Group VIII catalytic  
7 metals such as Fe, Ni, Co, Ru and Re, with cobalt being preferred.  
8 Additionally, a suitable catalyst may contain a promoter. Thus, a preferred  
9 Fischer-Tropsch catalyst comprises effective amounts of cobalt and one or  
10 more of Re, Ru, Pt, Fe, Ni, Th, Zr, Hf, U, Mg and La on a suitable inorganic  
11 support material, preferably one which comprises one or more refractory  
12 metal oxides. In general, the amount of cobalt present in the catalyst is  
13 between about 1 and about 50 weight percent of the total catalyst  
14 composition. The catalysts can also contain basic oxide promoters such as  
15 ThO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, MgO, and TiO<sub>2</sub>, promoters such as ZrO<sub>2</sub>, noble metals (Pt, Pd,  
16 Ru, Rh, Os, Ir), coinage metals (Cu, Ag, Au), and other transition metals such  
17 as Fe, Mn, Ni, and Re. Suitable support materials include alumina, silica,  
18 magnesia and titania or mixtures thereof. Preferred supports for cobalt  
19 containing catalysts comprise alumina or titania. Useful catalysts and their  
20 preparation are known and illustrated in U.S. Patent No. 4,568,663, which is  
21 intended to be illustrative but non-limiting relative to catalyst selection.

22  
23 The products as they are recovered from the Fischer-Tropsch operation  
24 usually may be divided into three fractions, a gaseous fraction consisting of  
25 very light products, a condensate fraction generally boiling in the range of  
26 naphtha and diesel, and a high boiling Fischer-Tropsch wax fraction which is  
27 normally solid at ambient temperatures.

28

#### 29 Hydrotreating to Remove the Oxygenates and Nitrogen

30

31 The wax and condensate recovered from the Fischer-Tropsch operation will  
32 contain varying amounts of oxygenates. Although the majority of the

1 oxygenates are concentrated in the condensate, sufficient oxygenates may be  
2 present in the wax to interfere with the oligomerization operation when an  
3 ionic liquid catalyst is employed. The majority of the oxygenates are in the  
4 form of alcohols, however, lesser amounts of ketones, aldehydes, carboxylic  
5 acids, esters, and anhydrides may also be present. As already noted above,  
6 the presence of oxygenates in the feed to the oligomerization operation will  
7 result in the deactivation of the ionic liquid catalyst. Aside from the alcohols  
8 present, the most important oxygenates appear to be ketones and carboxylic  
9 acids.

10  
11 In the present invention, the oxygenates present in the feed to the  
12 oligomerization operation, whether condensate or wax, are removed by  
13 hydrotreating. Hydrotreating also removes any nitrogen compounds which  
14 may present in the feed. The nitrogen content of the feed should be reduced  
15 to low levels (preferably less than 5 ppm) without excess cracking of the  
16 feedstock. "Hydrotreating" may be defined as a catalytic process, usually  
17 carried out in the presence of free hydrogen, in which the primary purpose  
18 when used to process conventional petroleum derived feed stocks is the  
19 removal of various contaminants, such as arsenic; heteroatoms, such as  
20 sulfur, oxygen, and nitrogen; and aromatics from the feed stock. In the  
21 present process, the primary purpose is to remove the oxygenates and  
22 nitrogen in the feed to the oligomerization operation. Generally, in  
23 hydrotreating operations, cracking of the hydrocarbon molecules,  
24 i.e., breaking the larger hydrocarbon molecules into smaller hydrocarbon  
25 molecules, is minimized. For the purpose of this discussion, the term  
26 "hydrotreating" refers to a hydroprocessing operation in which the cracking  
27 conversion is 20 percent or less.

28  
29 Catalysts used in carrying out hydrotreating operations are well known in the  
30 art. See, for example, U.S. Patent Nos. 4,347,121 and 4,810,357, the  
31 contents of which are hereby incorporated by reference in their entirety, for  
32 general descriptions of hydrotreating and of typical catalysts used in the  
33 process. Suitable catalysts include noble metals from Group VIIIA (according

1 to the 1975 rules of the International Union of Pure and Applied Chemistry),  
2 such as platinum or palladium on an alumina or siliceous matrix, and Group  
3 VIIIA and Group VIB metals, such as nickel-molybdenum or nickel-tin on an  
4 alumina or siliceous matrix. In carrying out the present invention,  
5 hydrotreating catalysts containing the metals nickel and molybdenum are  
6 especially preferred. U.S. Patent No. 3,852,207 describes a noble metal  
7 catalyst and mild conditions. Other suitable catalysts are described, for  
8 example, in U.S. Patent Nos. 4,157,294 and 3,904,513. The non-noble  
9 hydrogenation metals, such as nickel-molybdenum, are usually present in the  
10 final catalyst composition as oxides, or more preferably or possibly, as  
11 sulfides when such compounds are readily formed from the particular metal  
12 involved. Preferred non-noble metal catalyst compositions contain in excess  
13 of about 5 weight percent, preferably about 5 to about 40 weight percent  
14 molybdenum and/or tungsten, and at least about 0.5, and generally about 1 to  
15 about 15 weight percent of nickel and/or cobalt determined as the  
16 corresponding oxides. Catalysts containing noble metals, such as platinum,  
17 contain in excess of 0.01 percent metal, preferably between 0.1 and  
18 1.0 percent metal. Combinations of noble metals may also be used, such as  
19 mixtures of platinum and palladium.

20

21 The hydrogenation components can be incorporated into the overall catalyst  
22 composition by any one of numerous procedures. The hydrogenation  
23 components can be added to matrix component by co-mulling, impregnation,  
24 or ion exchange and the Group VI components, i.e., molybdenum and  
25 tungsten can be combined with the refractory oxide by impregnation,  
26 co-mulling or co-precipitation.

27

28 The matrix component or support can be of many types including some that  
29 have acidic catalytic activity; however, generally a non-acidic hydrotreating  
30 catalyst is preferred in carrying out the present invention, with alumina being  
31 especially preferred. Supports that have acidic activity include amorphous  
32 silica-alumina or may be a zeolitic or non-zeolitic crystalline molecular sieve.  
33 Examples of suitable matrix molecular sieves include zeolite Y, zeolite X and

1 the so-called ultra stable zeolite Y and high structural silica:alumina ratio  
2 zeolite Y such as that described in U.S. Patent Nos. 4,401,556; 4,820,402 and  
3 5,059,567. Small crystal size zeolite Y, such as that described in U.S. Patent  
4 No. 5,073,530, can also be used. Non-zeolitic molecular sieves which can be  
5 used include, for example, silicoaluminophosphates (SAPO),  
6 ferroaluminophosphate, titanium aluminophosphate and the various ELAPO  
7 molecular sieves described in U.S. Patent No. 4,913,799 and the references  
8 cited therein. Details regarding the preparation of various non-zeolite  
9 molecular sieves can be found in U.S. Patent Nos. 5,114,563 (SAPO) and  
10 4,913,799 and the various references cited in U.S. Patent No. 4,913,799.  
11 Mesoporous molecular sieves can also be used, for example, the M41S family  
12 of materials as described in J. Am. Chem. Soc., 114:10834-10843(1992),  
13 MCM-41; U.S. Patent Nos. 5,246,689; 5,198,203 and 5,334,368; and MCM-48  
14 (Kresge et al., Nature 359:710 (1992)). Suitable matrix materials may also  
15 include synthetic or natural substances as well as inorganic materials such as  
16 clay, silica and/or metal oxides such as silica-alumina, silica-magnesia, silica-  
17 zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary  
18 compositions, such as silica-alumina-thoria, silica-alumina-zirconia,  
19 silica-alumina-magnesia, and silica-magnesia zirconia. The latter may be  
20 either naturally occurring or in the form of gelatinous precipitates or gels  
21 including mixtures of silica and metal oxides. Naturally occurring clays which  
22 can be composited with the catalyst include those of the montmorillonite and  
23 kaolin families. These clays can be used in the raw state as originally mined  
24 or initially subjected to calcination, acid treatment or chemical modification.  
25  
26 In performing the hydrotreating operation, more than one catalyst type may be  
27 used in the reactor. The different catalyst types can be separated into layers  
28 or mixed.  
29  
30 Typical hydrotreating conditions vary over a wide range. In general, the  
31 overall LHSV is usually between about 0.5 to 5.0, preferably between about  
32 1.0 and 4.0. The total pressure ranging from about 200 psig to about  
33 2,000 psig. Hydrogen recirculation rates are typically greater than 50 SCF/Bbl,



1 and are preferably between 1,000 and 5,000 SCF/Bbl. Temperatures in the  
2 reactor will range from about 400 degrees F to about 800 degrees F (about  
3 205 degrees C to about 425 degrees C), with temperatures of less than about  
4 675 degrees F (about 360 degrees C) generally being preferred in the present  
5 process to avoid hydroisomerization.

6  
7 In practicing the present invention, during the hydrotreating step, the amount  
8 of the oxygenates are significantly reduced relative to the amount of  
9 oxygenates present in the Fischer-Tropsch derived feed entering the  
10 hydrotreating unit. As used herein, "significantly reduced" means that the  
11 elemental oxygen remaining in the hydrotreated feed is about 1500 ppmw or  
12 less. Preferably, substantially all of oxygenates are removed in the  
13 hydrotreating step. Using the present invention, the effluent from the  
14 hydrotreating operation preferably will contain less than about 200 ppmw  
15 elemental oxygen, even more preferably less than 100 ppmw elemental  
16 oxygen. However, while it is relatively easy to achieve these levels by  
17 hydrotreating the condensate, it has been found that more severe  
18 hydrotreating conditions may be required to reach these levels when the wax  
19 fraction is being treated. Consequently, as a practical matter, it may be  
20 desirable to allow oxygenate levels in excess of these preferred amounts to  
21 remain in the wax fraction and accept some deactivation of the ionic liquid  
22 oligomerization catalyst. The deactivation of the ionic liquid catalyst in this  
23 later instance requires that additional make-up catalyst be added to the  
24 oligomerization zone to replace the catalyst deactivated by the residual  
25 oxygenates.

26

#### 27 Thermal Cracking

28

29 The thermal cracking step employed in the process of the present invention is  
30 intended to crack the paraffin molecules in the Fischer-Tropsch feed into  
31 lower molecular weight olefins. Although Fischer-Tropsch wax and  
32 condensate usually contain a significant amount of olefins, in the present  
33 invention, most of the olefins are saturated in the hydrotreating operation.

1 Therefore, it is necessary to reintroduce sufficient olefins into the feed to allow  
2 for the oligomerization step to proceed.

3  
4 Although batch pyrolysis reactors such as employed in delayed coking or in  
5 cyclic batch operations could be used to carry out this step, generally a  
6 continuous flow-through operation is preferred in which the Fischer-Tropsch  
7 feed is first preheated to a temperature sufficient to vaporize most or all of the  
8 feed after which the vapor is passed through a tube or tubes. The conditions  
9 in the flow through reactor are critical to the optimal formation of olefins from  
10 the paraffins present in the substantially oxygenate-free Fischer-Tropsch  
11 derived feed. The temperature of the feed must be raised to a temperature  
12 sufficient to vaporize most or all of the feed. A desirable option is to bleed any  
13 remaining nonvaporized hydrocarbons prior to entering the cracking furnace.  
14 Liquid cracking has been found to lead to the formation of undesired paraffins.  
15 Preferably, the thermal cracking is conducted in the presence of steam which  
16 serves as a heat source and also helps suppress coking in the reactor. Details  
17 of a typical steam thermal cracking process may be found in U.S. Patent  
18 No. 4,042,488, hereby incorporated by reference in its entirety. Although  
19 catalyst is generally not used in carrying out the thermal cracking operation, it  
20 is possible to conduct the operation in a fluidized bed in which the vaporized  
21 feed is contacted with hot fluidized inert particles, such as fluidized particles of  
22 coke.

23  
24 In performing the thermal cracking operation, it is preferable that the feed be  
25 maintained in the vapor phase during the cracking operation to maximize the  
26 production of olefins. In the thermal cracking zone, the cracking conditions  
27 should be sufficient to provide a cracking conversion of greater than 10 weight  
28 percent of the paraffins present. The optimal temperature and other conditions  
29 in the thermal cracking zone for the cracking operation will vary somewhat  
30 depending on the feed. In general, the temperature must be high enough to  
31 maintain the feed in the vapor phase but not so high that the feed is  
32 overcracked, i.e., the temperature and conditions should not be so severe that  
33 excessive C<sub>4</sub> minus hydrocarbons are generated. The temperature in the

1 thermal cracking zone normally will be maintained at a temperature of  
2 between about 950 degrees F (510 degrees C) and about 1,600 degrees F  
3 (870 degrees C). The optimal temperature range for the thermal cracking  
4 zone in order to maximize the production of olefins from the Fischer-Tropsch  
5 feed will depend upon the endpoint of the feed. In general, the higher the  
6 carbon number, the higher the temperature required to achieve maximum  
7 conversion. Accordingly, some routine experimentation may be necessary to  
8 identify the optimal cracking conditions for a specific feed. The thermal  
9 cracking zone usually will employ pressures maintained between about  
10 0 atmospheres and about 5 atmospheres, with pressures in the range of from  
11 about 0 to about 2 generally being preferred. Although the optimal residence  
12 time of the feed in the reactor will vary depending on the temperature and  
13 pressure in the thermal cracking zone, typical residence times are generally in  
14 the range of from about 1.5 seconds to about 500 seconds, with the preferred  
15 range being between about 5 seconds and about 300 seconds.

16

#### 17 Oligomerization

18

19 Following pyrolysis, the olefin-enriched Fischer-Tropsch feed is oligomerized  
20 using a Lewis acid ionic liquid catalyst. The use of an ionic liquid catalyst for  
21 the oligomerization of the olefins in the present invention has certain  
22 *advantages over more conventional catalysts in that there is excellent mixing*  
23 *of the reactants with the catalyst resulting in short residence times and high*  
24 *yields, the oligomerization reaction takes place at relatively low temperatures,*  
25 *and the products are readily separated from the catalyst. In the present*  
26 *process, the olefin-enriched Fischer-Tropsch feed may be added to the*  
27 *catalytic mixture or the catalyst may be added to the feed. In either case, the*  
28 *feed and the product formed during oligomerization will form a separate phase*  
29 *from the ionic liquid which allows the two phases to be readily separated. In*  
30 *order to facilitate mixing of the ionic liquid catalyst and the feed, it is desirable*  
31 *to either stir the oligomerization mixture, bubble the feed through the ionic*  
32 *liquid catalyst, or use another type of reactor which facilitates good mixing of*  
33 *the catalyst and the hydrocarbon. Following completion of the oligomerization*

1 reaction, the mixing should be halted, and the product and residual feed  
2 should be allowed to form a distinct layer apart from the catalyst phase.

3  
4 The ionic liquid oligomerization catalyst used in this invention will be a Lewis  
5 acid catalyst and usually will comprise at least two components which form a  
6 complex. In most instances, the catalyst will be a binary catalyst, i.e., it will  
7 consist of only two components. The first component of the catalyst will  
8 usually comprise a Lewis acid selected from the group consisting of aluminum  
9 halide, alkyl aluminum halide, gallium halide, and alkyl gallium halide.

10 Preferred for the first component is an aluminum halide or alkyl aluminum  
11 halide. Aluminum trichloride is particularly preferred for preparing the  
12 oligomerization catalyst used in practicing the present invention. The  
13 presence of the first component should give the ionic liquid a Lewis (or  
14 Franklin) acidic character.

15  
16 The second component making up the catalyst is usually a quaternary  
17 ammonium or quaternary phosphonium compound, such as, for example, a  
18 salt selected from one or more of hydrocarbyl substituted ammonium halides,  
19 hydrocarbyl substituted imidazolium halide, hydrocarbyl substituted pyridinium  
20 halide, alkylene substituted pyridinium dihalide, hydrocarbyl substituted  
21 phosphonium halide. Preferred for use as the second component are those  
22 quaternary ammonium halides containing one or more alkyl moieties having  
23 from 1 to about 9 carbon atoms, such as, for example, trimethylamine  
24 hydrochloride, methyl-tributyl ammonium chloride, or alkyl substituted  
25 imidazolium halides, such as, for example, 1-ethyl-3-methyl-imidazolium  
26 chloride.

27  
28 The mole ratio of the two components will usually fall within the range of from  
29 about 1:1 to about 5:1 of said first component to said second component, and  
30 more preferably the mole ratio will be in the range of from about 1:1 to about  
31 2:1. The use of a binary catalyst composition consisting essentially of  
32 methyl-tributyl ammonium chloride and aluminum trichloride is particularly  
33 advantageous for carrying out the process of the present invention due to the

1 ease of preparation, the ready commercial availability of the components, and  
2 the relatively low cost.

3  
4 The amount of catalyst present to promote the oligomerization of the olefins  
5 should be not less than an effective oligomerizing amount, that is to say, the  
6 minimum amount of the catalyst necessary to oligomerize the olefins to the  
7 desired product. This may vary to some degree depending on the composition  
8 of the catalyst, the ratio of the two components of the catalyst to one another,  
9 the feed, the oligomerization conditions chosen, and the like. However, a  
10 determination of the effective catalytic amount should be well within the ability  
11 of one skilled in the art with no more than routine testing necessary to  
12 establish the amount needed to carry out the invention. As noted above,  
13 make-up catalyst added to the oligomerization zone may be necessary to  
14 replace catalyst that is deactivated by contaminants in the feed, mostly  
15 residual oxygenates present in the wax fraction. The amount of make-up  
16 catalyst necessary will depend on the amount of contaminants present.  
17 Preferably, the amount of contaminants will be low and the degree of  
18 deactivation of the catalyst also will be low. However, if the removal of the  
19 oxygenates to the most preferred levels during the hydrotreating step require  
20 operation at such high severity that significant cracking takes place and the  
21 amount of desirable high molecular weight products are correspondingly  
22 reduced, it may be necessary to tolerate some catalyst deactivation in order to  
23 produce the desired product slate.

24  
25 The oligomerization reaction takes place over a wide temperature range  
26 between the melting point of the catalyst and its decomposition temperature,  
27 preferably between about 120 degrees F and about 212 degrees F (about  
28 50 degrees C and about 100 degrees C).

29  
30 Following completion of the oligomerization reaction, the organic layer  
31 containing the Fischer-Tropsch derived oligomerization product is separated  
32 from the ionic liquid phase. Preferably, the oligomerization product will have  
33 an average molecular weight at least 10 percent higher than the initial

olefin-enriched Fischer-Tropsch feedstock, more preferably at least 20 percent higher. The acidic ionic liquid catalyst that remains after recovery of the organic phase is preferably recycled to the oligomerization zone.

### Dewaxing

The product from the oligomerization unit may require dewaxing to meet the lubricant base oil cold flow requirements. The dewaxing process may be a solvent or a catalytic process. Catalytic dewaxing is generally preferred, especially for the process schemes where some of the Fischer-Tropsch wax is hydroisomerized to lubricant base oil. In these schemes the catalytic dewaxing unit can operate in either of two modes, (1) feeding the oligomerization product or (2) feeding Fischer-Tropsch wax.

Catalytic dewaxing consists of three main classes, conventional hydrodewaxing, complete hydroisomerization dewaxing, and partial hydroisomerization dewaxing. All three classes involve passing a mixture of a waxy hydrocarbon stream and hydrogen over a catalyst that contains an acidic component to convert the normal and slightly branched iso-paraffins in the feed to other non-waxy species, such as lubricating base oil stocks with acceptable pour points. Typical conditions for all classes involve temperatures from about 400 degrees F to about 800 degrees F (about 200 degrees C to about 425 degrees C), pressures from about 200 psig to 3,000 psig, and space velocities from about 0.2 to 5 hr<sup>-1</sup>. The method selected for dewaxing a feed typically depends on the product quality, and the wax content of the feed, with conventional hydrodewaxing often preferred for low wax content feeds. The method for dewaxing can be effected by the choice of the catalyst. The general subject is reviewed by Avilino Sequeira, in *Lubricant Base Stock and Wax Processing*, Marcel Dekker, Inc., pages 194-223. The determination between conventional hydrodewaxing, complete hydroisomerization dewaxing, and partial hydroisomerization dewaxing can be made by using the n-hexadecane isomerization test as described in U.S. Patent No. 5,282,958. When measured at 96 percent, n-hexadecane conversion using conventional

1 hydrodewaxing catalysts will exhibit a selectivity to isomerized hexadecanes  
2 of less than 10 percent, partial hydroisomerization dewaxing catalysts will  
3 exhibit a selectivity to isomerized hexadecanes of greater than 10 percent to  
4 less than 40 percent, and complete hydroisomerization dewaxing catalysts will  
5 exhibit a selectivity to isomerized hexadecanes of greater than or equal to  
6 40 percent, preferably greater than 60 percent, and most preferably greater  
7 than 80 percent.

8  
9 In conventional hydrodewaxing, the pour point is lowered by selectively  
10 cracking the wax molecules mostly to smaller paraffins using a conventional  
11 hydrodewaxing catalyst, such as, for example, ZSM-5. Metals may be added  
12 to the catalyst, primarily to reduce fouling.

13 Complete hydroisomerization dewaxing typically achieves high conversion  
14 levels of wax by isomerization to non-waxy iso-paraffins while at the same  
15 time minimizing the conversion by cracking. Since wax conversion can be  
16 complete, or at least very high, this process typically does not need to be  
17 combined with additional dewaxing processes to produce a lubricating base  
18 oil stock with an acceptable pour point. Complete hydroisomerization  
19 dewaxing uses a dual-functional catalyst consisting of an acidic component  
20 and an active metal component having hydrogenation activity. Both  
21 components are required to conduct the isomerization reaction. The acidic  
22 component of the catalysts used in complete hydroisomerization preferably  
23 includes an intermediate pore SAPO, such as SAPO-11, SAPO-31, and  
24 SAPO-41, with SAPO-11 being particularly preferred. Intermediate pore  
25 zeolites, such as ZSM-22, ZSM-23, and SSZ-32, also may be used in carrying  
26 out complete hydroisomerization dewaxing. Typical active metals include  
27 molybdenum, nickel, vanadium, cobalt, tungsten, zinc, platinum, and  
28 palladium. The metals platinum and palladium are especially preferred as the  
29 active metals, with platinum most commonly used.

30  
31 In partial hydroisomerization dewaxing, a portion of the wax is isomerized to  
32 iso-paraffins using catalysts that can isomerize paraffins selectively, but only if

1 the conversion of wax is kept to relatively low values (typically below  
2 50 percent). At higher conversions, wax conversion by cracking becomes  
3 significant, and yield losses of lubricating base oil stock become  
4 uneconomical. Like complete hydroisomerization dewaxing, the catalysts  
5 used in partial hydroisomerization dewaxing include both an acidic component  
6 and a hydrogenation component. The acidic catalyst components useful for  
7 partial hydroisomerization dewaxing include amorphous silica aluminas,  
8 fluorided alumina, and 12-ring zeolites (such as Beta, Y zeolite, L zeolite). The  
9 hydrogenation component of the catalyst is the same as already discussed  
10 with complete hydroisomerization dewaxing. Because the wax conversion is  
11 incomplete, partial hydroisomerization dewaxing must be supplemented with  
12 an additional dewaxing technique, typically solvent dewaxing, complete  
13 hydroisomerization dewaxing, or conventional hydrodewaxing in order to  
14 produce a lubricating base oil stock with an acceptable pour point.

15

16 In preparing those catalysts containing a SAPO non-zeolitic molecular sieve  
17 and having a hydrogenation component for use in the present invention, it is  
18 usually preferred that the metal be deposited on the catalyst using a  
19 non-aqueous method. Catalysts containing SAPOs on which the metal has  
20 been deposited using a non-aqueous method have shown greater selectivity  
21 and activity than those catalysts which have used an aqueous method to  
22 deposit the active metal. The non-aqueous deposition of active metals on  
23 non-zeolitic molecular sieves is taught in U.S. Patent No. 5,939,349. In  
24 general, the process involves dissolving a compound of the active metal in a  
25 non-aqueous, non-reactive solvent and depositing it on the molecular sieve by  
26 ion exchange or impregnation.

27

28 For the purposes of the present invention, hydroisomerization dewaxing,  
29 especially complete hydroisomerization dewaxing, is preferred over  
30 hydrodewaxing if such operation is able to provide the desired viscosity and  
31 pour point specifications for the product. This is because with less wax  
32 cracking, the yield of lubricating base oil will be increased. The preferred



1 hydroisomerization catalyst for use in the catalytic hydroisomerization step  
2 comprises SAPO-11.

3

4 Hydrofinishing

5

6 Hydrofinishing operations are intended to improve the UV stability and color of  
7 the Fischer-Tropsch derived products recovered from the oligomerization  
8 zone. It is believed this is accomplished by saturating the double bonds  
9 present in the hydrocarbon molecule. A general description of the  
10 hydrofinishing process may be found in U.S. Patent Nos. 3,852,207 and  
11 4,673,487. As used in this disclosure, the term "UV stability" refers to the  
12 stability of the lubricating base oil or other products when exposed to  
13 ultraviolet light and oxygen. Instability is indicated when a visible precipitate  
14 forms or darker color develops upon exposure to ultraviolet light and air which  
15 results in a cloudiness or floc in the product. Lubricating base oils and diesel  
16 products prepared by the process of the present invention will require  
17 UV stabilization before they are suitable for use in the manufacture of  
18 commercial lubricating oils and marketable diesel.

19

20 In the present invention, the total pressure in the hydrofinishing zone will be  
21 above 500 psig and preferably above 1,000 psig. The maximum total pressure  
22 is not critical to the process; but due to equipment limitations, the total  
23 pressure will not exceed 3,000 psig and usually will not exceed about  
24 2,500 psig. Temperature ranges in the hydrofinishing zone are usually in the  
25 range of from about 300 degrees F (150 degrees C) to about 700 degrees F  
26 (370 degrees C), with temperatures of from about 400 degrees F  
27 (205 degrees C) to about 500 degrees F (260 degrees C) being preferred.  
28 The LHSV is usually within the range of from about 0.2 to about 2.0,  
29 preferably 0.2 to 1.5, and most preferably from about 0.7 to 1.0. Hydrogen is  
30 usually supplied to the hydrofinishing reactor at a rate of from about 1,000 to  
31 about 10,000 SCF per barrel of feed. Typically, the hydrogen is fed at a rate of  
32 about 3,000 SCF per barrel of feed.

1 Suitable hydrofinishing catalysts typically contain a Group VIII noble metal  
2 component together with an oxide support. Metals or compounds of the  
3 following metals are contemplated as useful in hydrofinishing catalysts include  
4 ruthenium, rhodium, iridium, palladium, platinum, and osmium. Preferably, the  
5 metal or metals will be platinum, palladium or mixtures of platinum and  
6 palladium. The refractory oxide support usually consists of silica-alumina,  
7 silica-alumina-zirconia, and the like. Typical hydrofinishing catalysts are  
8 disclosed in U.S. Patent Nos. 3,852,207; 4,157,294 and 4,673,487.

### 9 10 Distillation

11  
12 The separation of the Fischer-Tropsch derived products into the various  
13 fractions is generally conducted by either atmospheric or vacuum distillation  
14 or by a combination of atmospheric and vacuum distillation. Atmospheric  
15 distillation is typically used to separate the lighter distillate fractions, such as  
16 naphtha and middle distillates, from a bottoms fraction having an initial boiling  
17 point above about 650 degrees F to about 750 degrees F (about  
18 340 degrees C to about 400 degrees C). At higher temperatures, thermal  
19 cracking of the hydrocarbons may take place leading to fouling of the  
20 equipment and to lower yields of the heavier cuts. Vacuum distillation is  
21 typically used to separate the higher boiling material, such as the lubricating  
22 base oil fractions.

23  
24 As used in this disclosure, the term "distillate fraction" or "distillate" refers to a  
25 side stream product recovered either from an atmospheric fractionation  
26 column or from a vacuum column as opposed to the "bottom fraction" which  
27 represents the residual higher boiling fraction recovered from the bottom of  
28 the column. In this disclosure, the term "bottoms" also includes those bottoms  
29 fractions and bright stock derived from the oligomerization of olefins present in  
30 the Fischer-Tropsch feed streams.